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Review

Transpiring wall reactor in supercritical water oxidation

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A B S T R A C T

Reactor corrosion and plugging problems have hindered the commercialization of supercritical water oxidation (SCWO) for wastewater purification. The use of transpiring wall reactor (TWR) is an effective means to overcome the above two problems by forming a protective water film on the internal surface of the reactor to aviod contacting corrosive species and precipitated organic salts. This work mainly aims to objectively review experimental investigations and numerical simulation results concerning TWR. Subsequent investigations for parameters optimizations of TWR are also proposed in order to ultimately build effective regulation methods of obtaining excellent water film properties. All this information is very important in guiding the structure design and operation parameters optimization of TWR.

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Keywords: Supercritical water oxidation; Transpiring wall reactor; Corrosion; Plugging; Salt deposition

Contents

1.   Introduction

Supercritical water ($T > 374.15\,^{\circ}\text{C}$, $P > 22.12\,\text{MPa}$) has some unique properties such as high diffusion coefficiency, very low dielectric constant and viscosity, and small amounts of hydrogen bonds. Supercritical water can be regarded as a benign non-polar organic solvent, which is completely miscible with organic matter and oxygen, leading to no limitation of interfacial mass transfer resistance (Bermejo and Cocero, 2006b; Cabeza et al., 2011). Physicochemical properties of supercritical water have been objectively introduced in detail (Galkin and Lunin, 2005; Kruse and Dinjus, 2007). SCWO is a promising technology to deal with organic wastes, with this technology, organic wastes can be thoroughly oxidized and decomposed into harmlessly small molecular compounds such as CO_2, N_2, water under excess oxidant condition in single-phase supercritical water. Hetero-atoms in oragnic matters are mineralized into corresponding acids or inorganic salts, and the formation of nitrous oxides is inhibited owing to the low reaction temperatute. SCWO is particularly suitable for disposing organic wastewaters with high toxicity, high concentration and bio-refractory components. It can also recover energy and achieve heat self-sufficiency to ensure an economic advangtage (Veriansyah and Kim, 2007; Vadillo et al., 2011). When mass concentration of organic matters in feedstock is in the range of 3–4%, maintaining the whole reaction process commonly does not require an extra energy input process (Gidner and Stenmark, 2001; Griffith and Raymond, 2002). Furthermore, compared with incineration, SCWO does not have the problems of high cost, public resentment and secondary pollutants (Veriansyah and Kim, 2007) like dioxins formation (Kikuchi et al., 2011). Hence, SCWO has attracted much attention in the past three decades. To date, some pilot-scale plants and commercial plants have been employed to deal with different varieties of oragnic pollutants such as wastewaters and sewage sludge (Ma et al., 2003; Marrone et al., 2005; Bermejo and Cocero, 2006b; Marrone, 2013). However, harsh reaction conditions (high temperature, high pressure, excessive oxygen and corrosive ions, etc.) easily induce severe reactor corrosion problems, meaning a shorter reactor life and a poorer treatment result due to the formation of corrosion products. On the other hand, inorganic salts will precipitate in supercritical water due to its extremely low dielectric constant, which will result in reactor plugging owing to their deposition and further causes expensive and frequent shutdowns of the whole SCWO plant. These two key problems are still not effectively solved and seriously hinder the extensive commercialization of SCWO. Thus, pilot-scale and industrial-scale SCWO plants for real wastewater treatments are now still scarce (Marrone, 2013).

Wellig et al. (2009) think that reactor corrosion and plugging problems have to be solved by fluid dynamics and process engineering means utilizing a sophisticated apparatus and a processing. Hodes et al. (2004) also point out that the above problems can be accommodated by system designs and/or operational procedures. Kritzer (2004) reports that corrosion in supercritical water depended on solution properties (like density, temperature, pH value, electrochemical potential) and material characteristics (such as alloy composition, surface condition, material purity, heat treatment). It is difficult to find one material or design which can withstand all feed types under all operation conditions in SCWO (Kritzer et al., 1999a,b, 2000; Brunner, 2009). However, it has been proved that SCWO can be continuously operated for an acceptable period of time

via several effective methods to reduce the reactor corrosion rate. These corrosion control approaches include the use of high corrosion resistance material, liner, coating, employing transpiring wall/film-cooled wall reactor, adsorption/reaction on the fluidized solid phase, adopting vortex/circulating flow reactor, pre-neutralization, cold feed injection, feed dilution with non-corrosive wastes, effluent dilution/cooling, and optimization of operation conditions (Marrone and Hong, 2009). It is better to fix reaction conditions such as heteroatom types in feedstock, reaction temperature and pressure in order to select an appropriate reactor material. Generally speaking, nickel-base alloys show a benign corrosion resistance performance under supercritical conditions while titanium is good at subcritical conditions (Kritzer and Dinjus, 2001).

Hodes et al. (2004) have reviewed fundamental principles and studies on salt deposition and control in supercritical water. The options of avoiding reactor plugging include using specific reactor configurations and selecting suitable operation conditions, involving reverse flow tank reactor with a brine pool, transpiring wall reactor, reverse flow tubular reactor, centrifuge reactor, downflow type reactor, fluidized bed reactor, double wall stirred reactor, deep shaft reactor, and transpiring wall reverse-flow tank reactor, adsorption/reaction on a fluidized solid phase, high velocity flow, mechanical brushing, rotating scraper, reactor flushing, additives, low turbulence/homogeneous precipitation, crossflow filtration, density separation, and extreme pressure operation, etc. (Marrone et al., 2004; Brunner, 2009; Bermejo et al., 2006b; Obuse et al., 2006; Xu et al., 2010, 2012). Furthermore, Calzavara et al. (2004) set a moving surface and a stirrer in their reactor for salt deposition on it. Príkopský et al. (2007) install a protective metal sleeve replaced easily to prevent salts from depositing on the internal surface of their axial reactor. However, no one reactor design or operation mean has been proved to be obviously superior to the others in all aspects.

Nowadays, it seems that the most effective approach to overcoming reactor corrosion and plugging is to design an appropriate reactor. Reactor configuration design is considered as the key problem of SCWO commercialization (Brunner, 2009). Although tubular reactor is most widely used due to its simplicity and reliability properties, it is not fit to dispose high salt-containing feedstock or highly corrosive feedstock (Vadillo et al., 2011). Moreover, rapid exothermic reactions may result in uncontrolled hot spots. It is very expensive to coat the high-temperature and high corrosion resistant material on the inner surface of the tubular reactor. Corrosion and plugging problems are still big risks in the real operation, and even make commercial SCWO plants inactive (Marrone, 2013).

Herein, TWR has become a very important selection in SCWO (Kawasaki et al., 2006; Bermejo et al., 2006b; Bermejo and Cocero, 2006a; Gong et al., 2009; Gong and Duan, 2010; Zhang et al., 2011b), which is even regarded as the most promising reactor construction (Kritzer and Dinjus, 2001; Bermejo and Cocero, 2006b). As elucidated in Fig. 1. TWR is mainly composed of a pressure-bearing wall and a porous transpiring wall (a non-load-bearing reaction chamber). It perfectly solves the corrosion and plugging problems by forming a protective transpiration water film on the inner surface of the porous transpiring wall to prevent corrosive species and precipitated salts from contacting the reactor inner surface (Wellig et al., 2005; Zhang et al., 2010; Xu et al., 2010). TWR has a promising future so that many researchers have paid much
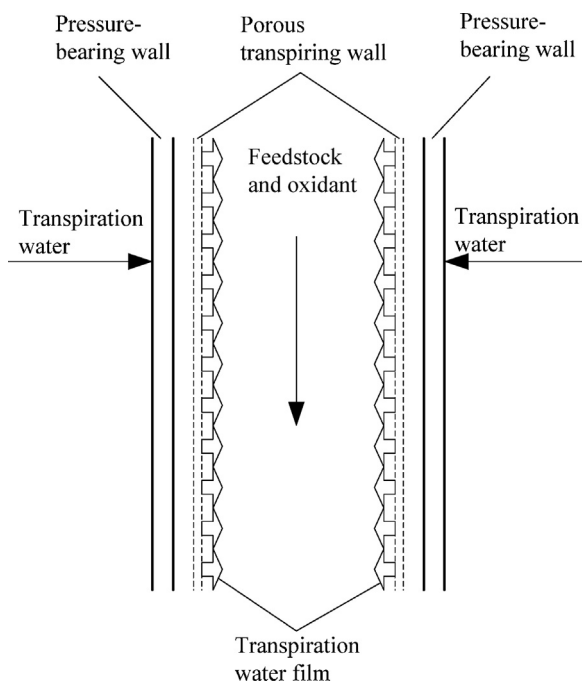
Fig. 1 – Basic structure of TWR.

attention on it. Numerous TWR designs have been developed and patented, as shown in the reports of Bermejo and Cocero (2006b) and Bermejo et al. (2006a). TWR has been extensively investigated by developing transpiring wall structures and materials, disposing different wastewaters with high salt contents, and using different preheating systems (Bermejo et al., 2011). For instance, TWR is employed to work for the U.S. Army in Sandia's EER, Pine Bluff Arsenal (Rice et al., 2000) and in trials for the waste destruction of Blue Grass Chemical weapons (Ahluwalia et al., 2001). Príkopský et al. (2007) have summarized the characteristics of several varieties of TWR tested by various research institutions such as Foster Wheeler Development Corp., Sandia National Labs., Aerojet GenCorp Inc., Forschungszentrum in Karlsruhe, and Swiss Federal Institute of Technology. A full-scale SCWO-TWR system has been designed and operated at different parameters and conditions such as different transpiration water temperatures, feed pH, and turbulence in the reactor (Foster Wheeler, 2001).

So far, there have been many studies and few relevant reviews (Bermejo and Cocero, 2006b; Zhang et al., 2011b) concerning TWR, so a more systematic and deeper summarization on TWR is very necessary and valuable. This work aims to provide more insight into TWR characteristics based on a systematic and thorough review of the previous experiments and simulation investigations. It mainly involves TWR's construction properties, combination with a hydrothermal flame, influences of operation parameters, utilization and optimization of operation parameters, safety control, economic evaluation and numerical simulations. The current problems on TWR are also analyzed and subsequent, in-depth work required to be conducted in the TWR development and application is proposed.

## 2.   Experimental investigations into TWR

2.1.   Construction properties

Tube reactor will plug and erode when disposing organic solution with inorganic salts and/or acids (Abeln et al., 2004), but

TWR has a good potential to avoid them because of its special configuration. Clean water flows across the small pores of the porous transpiring wall and forms a cool, protective transpiration water film against corrosive species, precipitated salts and high temperatures. Transpiration water film does protect the porous wall from corrosion and salt buildup, because significant corrosion and salt buildup are not found in TWR tests by post-test visual inspection and analysis of metals in liquid effluent (Foster Wheeler, 2001). For different feedstocks even with 10 wt% salt content, minimal or no evidence of corrosion is found in the area protected by transpiration water (Marrone and Hong, 2009). It is also observed that the temperature near the transpiring wall (pore size > 24 μm) is 20–50 °C lower than the reaction temperature, so the transpiring wall can protect itself under high temperature conditions (Bermejo et al., 2006a). Bermejo et al. (2006b) have summarized the transpiring wall forms and their working principles. They point out that in general, transpiring wall can be classified into two forms, namely, a sintered form by different materials (like stainless steel, Ni-alloy, alumina ceramic) and an element consisting of many thin layers or platelets bonded together. However, the latter is not easily removable and exhibits a mechanical integrity problem during its test processes (Marrone and Hong, 2009). Fauvel et al. (2005) chose pure α-alumina as transpiring wall material and confirmed that alumina sensibility to thermal gradient was not a limiting factor of reactor operation.

The cooler transpiration water can decrease the pressure-bearing wall temperature and meanwhile ensure a higher reaction temperature in the reactor center. This helps to improve waste destruction kinetics but creates a risk of incomplete waste destruction near the transpiring wall. However, none of the related investigations into these SCWO-TWR systems have indicated a poor destruction efficiency (Marrone and Hong, 2009). Furthermore, owing to the protection of transpiration water, both the transpiring wall and the pressure-bearing wall can employ the relatively cheap material. TWR usually has a temperature gradient, and its upper and middle zone is commonly a supercritical zone for oxidation reaction, but the bottom is often a subcritical zone to minimize salts deposition (Plugatyr and Svishchev, 2008; Bermejo et al., 2010). Haroldsen et al. (1996) point out that transpiring wall can almost remove the deposited salts on the reactor surface, except from the heating section of the reactor top. Príkopský et al. (2007) further comfirm that inorganic salts will deposite on the reactor upper hot zone which was above the protective transpiring wall section. Bermejo et al. (2010) prove that the porous wall on the reactor upper cup has very little effect on reactor performances, so it is preferable to construct this part of reaction chamber using a non-porous, more durable material. However, it is noticed that the upper section of the platelet liner (a transpiring wall form) undergoes severe corrosion and salt deposition problems without the protection of transpiration water (Foster Wheeler, 2001). In addition, back-mixing will lead to the corrosion of the TWR injection part made of Hastelloy C-276 (Lee et al., 2005). Hence, the configuration of the heating section of the reactor top is crucial. Abeln et al. (2007) also notice that their TWR is subjected to corrosion to some extent when conducting dyeing wastewater SCWO experiments. Salts deposition at the reactor entrance and on inner porous ceramic wall was detected in another report (Gong et al., 2009). These phenomena are attributed to the interruption or blockage of transpiration water, because this situation will leave the transpiring wall or the reactor
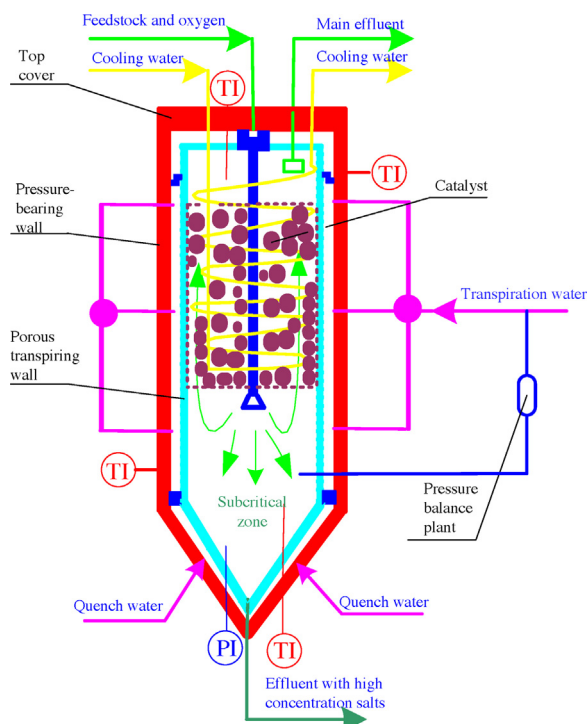
Fig. 2 – Schematic diagram of a novel TWR construction (Xu et al., 2012).

inner wall exposed to severe corrosive species, precipitated salts as well as high temperatures. Therefore, it can be considered that the biggest risk of employing a TWR is the loss of transpiration water, even if it is deprived from a small section of the transpring wall. It is essential to form an excellent transpiration water film with suitable thickness, homogeneous and stable distribution, depending on the TWR construction and operation parameters and determines reactor performances to a great extent (Gong et al., 2007b, 2008; Shen et al., 2010; Zhang et al., 2011a).

As is shown in Fig. 2, a novel TWR has been developed, combining the advantages of both the Modar reactor (Hong et al., 1989) and a traditional TWR to minimize the reactor corrosion rate and plugging risk (Xu et al., 2010). The reactor has been successfully used in a pilot-scale SCWO plant to dispose sewage sludge or organic wastewaters (Xu et al., 2012). The removal efficiencies of COD (chemical oxygen demand) and NH_3-N (ammonia nitrogen) can reach up to 99.65% and 96.50% for sewage sludge, and 99.83% and 98.85% for pesticide wastewater, respectively. This TWR belongs to a reverse flow tank reactor, and it can also load some necessary catalysts if they are required in the reaction processes (Xu et al., 2010). Inorganic salts in reaction fluid precipitate at the supercritical condition and fall down into the subcritical zone to re-dissolve. The subcritical zone at the bottom of the reactor is formed by pumping quench water. The main reactor effluent flows out from the reactor top outlet, and a small amount of effluent with high concentration salts discharges from the reactor bottom outlet (Xu et al., 2012). Additionally, possible surplus energy in SCWO can be recovered in the form of hot water or steam by the cooling spiral coil. However, it is found that only 83.6 wt% salts can be recovered from the reactor effluent. This is consistent with the previous report that not 100% salts are recovered from reactor effluent (Fauvel et al., 2003a, 2004; Abeln et al., 2004). The rest of salts should deposit in the preheating section of the plant as well as in the

reactor inlet pipelines. The plugging problem and corrosion indicators are not found in operation processes, but periodical cleaning seems to be necessary. According to the tests, the pressure difference of two sides of the transpiring wall is stable, and no plugging and breakage phenomena take place in operation processes. The SCWO-TWR plant can continuously and stably run at least more than 72 h after started.

2.2. Combination with a hydrothermal flame

The hydrothermal flame is a new method of combustion that takes place in SCWO reactions when the temperature is higher than the auto-ignition temperature (Cabeza et al., 2011). Liquid fuel such as methanol, alcohol or isopropyl alcohol (Bermejo and Cocero, 2006a; Bermejo et al., 2008), is introduced into the reactor through a separate pipeline to combust with oxygen to compensate heat requirement. Augustine and Tester (2009) have systematically reviewed hydrothermal flames from phenomenological experimental demonstrations to quantitative understanding. They have found that hydrothermal flames are characterized by very high reaction temperatures (usually in excess of 1000 °C) and extremely fast oxidation rates (on the order of only 10–100 ms). It is attributed to that the extremely high temperature can obviously decrease the reaction time of reactants for the same removal efficiency of organic matter, making even only 0.1 s be enough at a subcritical temperature of feedstock injection (Wellig et al., 2009). Thus, the reactor volume can be reduced evidently, meaning a remarkably low reactor investment. However, SCWO without a hydrothermal flame in the reactor requires an external heat source such as an electric heater or a gas-fired heater. This process has a moderate reaction temperature (450–650 °C) and longer residence times ranging from several seconds to minutes (Augustine and Tester, 2009).

The hydrothermal flame is usually used as an internal heat source. It can decrease the corrosion and plugging problems of reactor inlet lines in SCWO, because it provides desired reaction temperatures operating at low feed temperatures (Narayanan et al., 2008). Inlet feed will not require to be preheated up to reaction temperatures above the critical point as in traditional SCWO processes (Augustine and Tester, 2009). Bermejo et al. (2011) present that it is possible to initiate the reaction with feed injection temperatures close to room temperature when using vessel reactors. SCWO with a hydrothermal flame permits the construction of smaller reactors, and higher operation temperatures also improve the energy recovery (Augustine and Tester, 2009). Thus, SCWO with a hydrothermal flame has many advantages compared with the flameless process. These advantages help to overcome the traditional challenges, and make the commercialization of SCWO successful and profitable (Cabeza et al., 2011).

Many researchers have probed the feasibility of TWR with a hydrothermal flame to solve corrosion and plugging problems in SCWO. It is found that TWR with a hydrothermal flame can obtain an extremely high temperature up to 800–1200 °C (Wellig et al., 2005). Wastewater is pumped over the flame to be preheated and then reacts with oxygen, so feedstock even does not require to be preheated and can enter the reactor directly (Wellig et al., 2005). However, a specific reactor configuration is required so that the pressure-bearing wall can work with such a high temperature flame (Serikawa et al., 2002; Wellig et al., 2005; Príkopský et al., 2007). In general, a porous transpiring wall element is adopted to enclose the reaction

fluid and form the reaction chamber, and cool transpiration water is pumped into the reactor so as to low the temperature of the pressure-bearing wall. Thus, the harshest reaction environment is confined in the reactor which is protected by a transpiring wall.

The research group in ETH first explores the hydrothermal flame in a TWR to improve SCWO performances (Rudolf vonrohr et al., 2008) and have successfully investigated, designed and operated a TWR with a hydrothermal flame. Wellig et al. (2009) conduct experimental studies by combining the advantages of hydrothermal flame with the protection action of transpiring wall. In this combination, the hydrothermal flame is used to remove organic matters in the wastewater feed, while the TWR can inhibit corrosion and plugging of reactor in the hydrothermal flame reaction systems. This kind of TWR exhibits a good performance in destructing artificial wastewater with a salt content up to 3 wt%, and the sustaining of a stable hydrothermal flame in supercritical water is regarded as a key feature (Rudolf vonrohr et al., 2008). Príkopský et al. (2007) also confirm that 65% Na_2SO_4 with an initial concentration up to 3 wt% is detected in this reactor effluent and no plugging was observed. Other researchers also have clarified that this kind of TWR can overcome corrosion and salt deposition problems in the preheating pipelines as well as in the reactor inlet (Wellig et al., 2005, 2009; Sierra-Pallares et al., 2009).

In this TWR, waste injection at a subcritical temperature has become a significant aspect in a novel reactor design (Bermejo et al., 2009a,b). Steady operations are possible at the flame regime and at a subcritical injection temperature, and ignition will happen in the reaction chamber but not in the injector, meaning it is very convenient to inject feed with a high salt content (Bermejo et al., 2011). Bermejo et al. (2011) further prove that the fluid velocity in the reactor determined the minimum injection temperature and the injection temperature can be even as low as 170 °C when the fluid flow velocity was below 0.04 m/s. It is also confirmed that the reactions can be initiated even by injecting the feed at a temperature as low as 150 °C when using a TWR with a tubular mixer and a back mixing area at its top (Bermejo et al., 2006b). Besides, Narayanan et al. (2008) have examined the ignition and extinction process, flame properties, temperature profiles, and influences of inorganic salts over a broad range of operation conditions. Wellig et al. (2005) also check the influence of the intensity (i.e., mass flow rate) and temperature of transpiration water on TWR performances, and find that the methanol conversion rate is higher than 99% even in a relatively low transpiration water temperature range of 125–250 °C. Of course, adopting a hydrothermal flame in a TWR requires studying the influences of feed flow rate, injection temperature, the size of the injector and so on by the detections of reactor temperature profiles and TOC (total organic carbon) removal efficiencies. This is because it requires ensuring appropriate temperature distribution and flow field distribution to stabilize the hydrothermal flame and gain a desired pollutants removal efficiency. It is very important to design a proper injector (burner) configuration and operate the reactor at appropriate conditions to achieve above aims. It is necessary to investigate ignition and extinction limits, removal efficiencies of organic matter, and flame stability in this variety of TWR (Wellig et al., 2005, 2009; Narayanan et al., 2008; Sierra-Pallares et al., 2009).

2.3. Operation parameters

2.3.1. Influence of parameters on TWR

It is believed that operation parameters influence the interactions (like heat transfer and mass transfer) between transpiration water film and reaction fluid, the actions (such as dilution, washing, and dissolution actions) of water film, and the romoval rate of oragnic matters, so they play significant roles in the formation processes and final performances of transpiration water film. Different SCWO-TWR systems have various technical solutions for reagent preheating, cooling, and flow control across the transpiring wall, and a detailed introduction has been provided elsewhere (Bermejo et al., 2006a). Some researchers recommend utilizing oxygen instead of air, increasing the transpiration water temperature to reduce thermal stress, and altering water flow circuitry in the transpiring wall (Foster Wheeler, 2001). Gong et al. (2007a) advise pre-treating feedstock to reduce salt content, mixing wastewater and oxidant in the reactor directly, and adding clean water or alkali solution to neutralize formed acids to reduce corrosion, to cool the effluent temperature and to re-dissolve precipitated salts. Bermejo et al. (2010) systematically examine the influence of different operation parameters on TWR performance indexes, and claim that material durability, energy saving, reactor productivity and X_{TOC} determine the operation conditions. The feed temperature has a direct role in TOC removal, but the air temperature has a negligible influence (Bermejo et al., 2006b). They further clarify that transpiring wall parameters have slight effect on X_{TOC}, and propose using periodical cleaning and recirculation of reactor effluent as transpiring flow to avoid the fouling problem of transpiring wall (Bermejo et al., 2006a).

Zhang et al. (2012) develop a pilot-scale SCWO-TWR plant and optimize process parameters according to temperature profiles and gas–liquid products. They believe that increasing the inlet temperature of the upper branch of transpiration water can improve TOC removal. The findings in a TWR for SCWO of acrylonitrile manufacturing wastewater display that with the increasing of reaction temperature and the residence time, TOC conversion also increases, but it is hardly affected by excess oxygen and initial TOC concentration. It is different from Gong et al.'s conclusion (2009) that the destruction efficiency of organic matters increases with OC (oxidation coefficient). Lee et al. (2005) also prove that increasing reaction temperature and OC can completely convert halogenated organic compounds with a higher concentration by SCWO in a TWR. Transpiration water intensity (R) is defined as the ratio of the mass flow rate of transpiration water to the bulk mass flow rate at the TWR entrance (Príkopský et al., 2007). R can be considered as one of the most significant operation parameters, which can reflect the flow rate of transpiration water. It has a great influence on water film performances and reaction temperature, and even determines the whole reactor performances. A high R is helpful for the protection action of the water film, but may evidently dilute feedstock, and decrease the residence time and the reaction temperature (Zhang et al., 2012), so it needs to select a proper R value in a real operation process. It has been confirmed that R (0.04–0.08) has minor influence on the temperature profiles and feed degradation, meaning that the mixing and cooling effect of transpiration water can be offset within the above range (Zhang et al., 2012). The lower transpiration water temperature is beneficial to the protection of the transpiring wall (Zhang et al., 2010).

The cooling action of transpiration water is more remarkable in the case of a low feed flow rate, and increasing the flow rate of transpiration water decreases the useful length of the reactor. Thus, it needs to ensure a satisfactory destruction efficiency at a lower flow rate of transpiration water condition. Moreover, fluid flow velocity determines the extinction temperature of the hydrothermal flame, and the higher flow velocity will result in a thinner wall boundary layer (Foster Wheeler, 2001).

2.3.2. *Utilization and optimization of parameters in TWR*

Main operation parameters should have a complicated coupling relationship with the water film performances indexes, mainly including thickness, distribution uniformity and stability. Selecting suitable operation parameters is very important to achieving the protective action of transpiration water film. In general, typical SCWO operation conditions are commonly 500–650 °C, 25–30 MPa with a residence time under one minute, as well as organic matter concentrations of 1–20 wt% (Marrone, 2013). In fact, many researchers control the operation pressure at approximately 25 MPa (Shin et al., 2009; Wang et al., 2011; Bamban et al., 2011; Sögüt et al., 2011; Zhou et al., 2013) because a high value will accelerate reactor corrosion (Kritzer, 2004). TWR can even dispose organic wastewater even with 30 wt% organic matters under the conditions that the reaction temperature of higher than 700 °C, the residence time of 120 s, and OC = 2.0. Some investigators have studied kinetics for several types of organic wastewaters SCWO under different conditions in TWRs. As elucidated in Table 1, it can be seen that the reaction orders of wastewater and oxidant are almost first and zero, respectively. According to the kinetics information, researchers can regulate the reaction rate, control products distributions and conduct reactor design.

Crooker et al. (2000) have designed two SCWO-TWR plants, of which one is employed to deal with excess hazardous materials from Navy ships at 24.1 MPa, 594–816 °C and using air as oxidant. X_{TOC} can approach 99.99% and the corresponding TOC value is below 3.5 mg/L. Another one is designed for the destruction of obsolete, colored smokes/dyes and pyrotechnic munitions at 26.3 MPa, 575–750 °C, utilizing oxygen as oxidant. Abeln et al. (2007) conduct dyeing wastewater SCWO in a TWR at 750 °C, and X_{TOC} is higher than 99.6% and the corresponding TOC concentration is lower than 100 mg/L. Gong and Duan (2010) report that X_{COD} is about 99.23% when landfill leachate is treated in a SCWO-TWR plant at 430 °C and 30 MPa. X_{COD} can be more than 99% when high concentration acrylic acid wastewater is handled at 450 °C, 34.3 s and OC = 1.2 (Gong et al., 2007a). It is also found that X_{COD} and the color removal rate were 98.4% and 99.9% at 431 °C, 28 MPa with a residence time less than 35 s for reactive dye wastewater SCWO in a TWR (Gong et al., 2007a,b,c). It is suggested that the feed temperature should be controlled at 350–400 °C, and the middle branch of transpiration water temperature should be in the range of 200–300 °C in order to ensure X_{TOC} of higher than 99.9% and harmless gas effluent (Zhang et al., 2011a). Bermejo et al. (2006a) optimize their TWR operation conditions at a feed flow of 16 kg/h, feed inlet temperatures higher than 300 °C, R = 0.2–0.6, and 8 wt% isopropanol as a fuel. Additionally, in the SCWO-TWR plant of Lee et al. (2005), feed solution and oxidant are heated to 400–450 °C and transpiration water is preheated to 350–400 °C. The researchers in ETH control a concentrated aqueous stream of methanol in the temperature range of 200–350 °C (Wellig et al., 2009), and the

Table 1 – Kinetics parameters of several organic wastewaters SCWO in TWR.

Feedstock	Reaction conditions	Pre-exponential factor, A	Activation energy, E_a	Reaction order		Reference
				Wastewater	Oxidant	
Industrial dyeing wastewater	322–431 °C, 18–30 MPa, OC: 0.6–2.0	1.07 s^{-1}	12.12 kJ mol^{-1}	1	0	Gong et al. (2008)
Acrylic acid production wastewater	350–450 °C, 18–32 MPa, 10–40 s, OC: 0–2.0	4.97 s^{-1}	20.64 kJ mol^{-1}	1	0	Gong et al. (2009)
Landfill leachate wastewater	320–430 °C, 18–30 MPa, 17.2–38.8 s	34.86 s^{-1}	32.1 kJ mol^{-1}	1	0	Gong and Duan (2010)
Acrylonitrile wastewater	299–552 °C, 25 MPa, 3–30 s, OC: 0.5–2.5	$6.07(\pm6.89) \times 10^3$ mol$^{-0.26}$ s^{-1}	66.33($\pm$5.87) kJ mol^{-1}	1.26($\pm$0.15)	0.00($\pm$0.15)	Shin et al. (2009)

fuel stream with 27 wt% methanol can be even below 100 °C (Wellig et al., 2005). The high feed concentration is beneficial to feed degradation due to the high reaction temperature gained by reaction heat release. Bermejo et al. (2005) have verified that a high isopropyl alcohol concentration can reduce feed and transpiration water temperatures, even without preheating transpiration water and air. X_{TOC} can be near 100% in the case of the feed flow rate of 16.5 kg/h, the transpiration water temperature of 200 °C, the air inlet temperature of 300 °C, the isopropyl alcohol concentration of 8 wt% and R = 0.5.

The operation characteristics of TWR have been extensively tested by many institutions. Bermejo et al. (2006a) have summarized major patents, characteristics and operation parameters regarding these TWRs. As an extension, Table 2 further supplements some new important information and illustrates their major construction characteristics and operation conditions. It can be observed TWR can obtain very high removal efficiencies for model compounds or real wastes. It can avoid the plugging problem but fails to recover all of salts introduced from feedstock (Abeln et al., 2001; Lee et al., 2005; Príkopský et al., 2007). Furthermore, it is also verified that TWR has a good corrosion resistance property in SCWO (Haroldsen et al., 1996; Abeln et al., 2000; Fauvel et al., 2005; Turbosystems Engineering, 2008a,b; Xu et al., 2012) because the concentrations of iron, nickel, chromium ions in the reactor effluent are very low.

As indicated in Table 2, all of TWRs have a porous element for forming the reaction chamber, but have different feedstock preheating temperatures and the flow rate controls, etc. The porous wall can consist of different materials or styles. The most frequently adopted one is the sintered metal wall made of stainless steel or nickel-base alloy. This porous wall is commonly made by the method that metal powder or many layers metal nets is sintered at a high temperature in a model. Nevertheless, Bermejo et al. (2006a) report that the sintered stainless steel or nickel-base alloy 600 wall should work at below 600 °C, or it will be damaged. The porous platelets format has been proved to be very effective (Bermejo et al., 2006a), which is usually supplied by Aerojet in USA. Each platelet is etched with a specific pattern of indentations so that a three-dimensional network of channels can be formed when many platelets are combined together (Bermejo and Cocero, 2006b). However, Ahluwalia et al. (2001) find some minor problems (breakage and deformation) related to the durability of this transpiring wall.

Transpiration water can be either subcritical water or supercritical water, but its temperature is commonly lower than that of the reaction fluid in the reactor center. Subcritical water film can continuously dilute, re-dissolve and/or sweep precipitated salt particles and corrosive species away from the internal surface of the transpiring wall. However, it dilutes hot reaction fluid and evidently reduces the reactor effluent temperature, making heat recovery less favorable (Bermejo and Cocero, 2006b). Supercritical water film does not have the re-dissolving action, probably resulting in slight corrosion and salt deposition problems on the transpiring wall. In general, transpiration water can be controlled at a subcritical temperature (<250 °C) for a TWR with a hydrothermal flame and a supercritical temperature (350–450 °C) for a TWR without a hydrothermal flame, as illustrated in Table 2. It is better to maintain a low velocity of transpiration water and distribute it uniformly in order to form an excellent transpiration water film (Xu et al., 2010, 2012). Zhang et al. (2011b) also propose

to optimize operation parameters such as the temperature and the flow rate of transpiration water to create a uniform transpiration water film. Of course, due to a weak mechanical strength of the transpiring wall, the pressure difference of its two sides must be monitored and controlled in an appropriate range in the real operation (Fauvel et al., 2004; Zhang et al., 2011b).

Additionally, an anticipated reactor temperature distribution should be accomplished for the reaction and safety control processes. The temperature of the subcritical zone as a brine pool can be controlled in the range of 350–370 °C by quench water according to the salts solubilities reported in the previous studies (Hodes et al., 2004; Stendahl and Jäfverström, 2003; Príkopský et al., 2007). The bases such as K_2CO_3, $KHCO_3$, KOH are suitable for being utilized as neutralization agents in SCWO, but NaOH is unsuitable due to its precipitation properties (Kawasaki et al., 2007). Periodical cleaning is also proposed for the TWR in the real operation (Fauvel et al., 2003b; Bermejo et al., 2006a) due to incomplete salts recovery.

2.3.3. Further investigations for parameters optimization

It can be supposed that the formation of transpiration water film may have two kinds of pathways. The first one may be that low flow rate transpiration water flows through the transpiring wall with the smaller pore sizes, thus forming a thinner homogeneous water film after diffusing on the inner surface. Another pathway may be that the higher flow rate transpiration water is pumped into the reactor and yields jet flows when getting across the bigger size pores on the transpiring wall, and then is connected together by the gravity action to form a thicker and unhomogeneous water film. The functions of reducing reactor corrosion rate and salt deposition problems are completed mainly by the dissolution, dilution and/or washing action of water film (Marrone et al., 2004; Brunner, 2009). However, their separate contribution is now still unclear. The operation conditions of forming the above three actions are different, so this has significant influence on the operation parameters selection and the transpiration water film performance optimization. Thus, detailed formation process and actions of the transpiration water film still reqiure further exploration.

It has been verified that the material, pore size and construction of the transpiring wall have neglectable effect on X_{TOC}, and the construction design of the transpiring wall can reduce the effect of transpiration water flow rate on the reaction temperature profile (Bermejo et al., 2006a). Further investigations illustrate the influence of feedstock flow rate, feedstock temperature, transpiration water flow rate, transpiration water temperature, oxidant entrance temperature and fuel on X_{TOC} and temperature profile (Bermejo et al., 2006b). The feedstock flow rate and the ethanol concentration have remarkable effect on the reactor temperature profile. The high feedstock temperature, feedstock flow rate and ethanol concentration help to remove ethanol, but weaken the protection action for the upper transpiring wall, so feedstock conditions are optimized at 380 °C and 0.002–0.003 kg/s (Zhang et al., 2010). Lieball (2003) convinces that natural convection and nonlinear characteristics decrease the thickness of protective water film. According to the above and previous summarizations, present investigations mainly involve the influence of feedstock flow, feedstock temperature, transpiration water flow rate, transpiration water temperature, etc., on the reactor temperature profile and the removal efficiency of

Table 2 – Main construction characteristics and operation parameters of TWR.

Organism	Construction characteristics	Operation conditions	Results	References
Swiss Federal Institute of Technology (ETH) (Switzerland)	Diameter = 22 mm Thickness = 3.75 mm Length = 50 + 325 mm (combustion chamber + porous reaction zone) Material: Porous sintered alloy 625 (3 μm) Oxidant: O_2 T. Flow: water	t_R = 50–100 ms (combustion chamber) Feed = 5.4 + 3.6 kg/h (fuel + waste) F_T = 5 kg/h T_R = 700 °C P = 25 MPa T_{FT} = 40–250 °C	Methanol, artificial wastewater with 3 wt% Na_2SO_4, X_{TOC} > 99.9%, no plugging problem	Wellig et al. (2005) and Príkopský et al. (2007)
Foster Wheeler Development Corporation (USA)[a]	Diameter = 152 mm Length = 1600 mm Material: Alloy 600 (several thin platelets are bonded together) Oxidant: air T. Flow: high-purity water	Feed = 113–227 kg/h F_T = 381–417 kg/h T_R = 594–816 °C P = 24.1 MPa	Navy shipboard wastes, X_{TOC} > 99.99%, (TOC < 3.5 mg/L), no obvious corrosion or salt deposition	Crooker et al. (2000) and Marrone and Hong (2009)
Institute of Technical Chemistry (ITC-CPV) (Germany)	Diameter = 60 mm Length = 950 mm Material: porous sintered stainless steel (30 μm) Oxidant: air T. Flow: water	Feed = 5–20 kg/h Air = 40 kg/h F_T = 30 + 50 kg/h (T. Flow + Quench) T_R = 630 °C P = 32 MPa T_{FT} = 550 °C	Ethanol, paper mill waste effluents, X_{TOC} = 99.9%	Abeln et al. (2004, 2007)
Manufacturing Engineering R&D Institute (Korea)	Material: porous ceramic Oxidant: H_2O_2 (sprayed into the reactor) T. Flow: water + NaOH solution	Feed = 1 kg/h P = 25 MPa T_R = 340–440 °C T_{FT} = 350–400 °C	2,4-Dichlorophenol, removal efficiency of 88.9–98.7%	Lee et al. (2005)
Zhongyuan University of Technology (China)[a]	Diameter = 9 mm Length = 500 mm Material: porous ceramic tubes Oxidant: H_2O_2 T. Flow: water	T_R = 440 °C P = 28 MPa F_T = 1.0 kg/h T_R = 38.8 s	Landfill leachate, X_{COD} = 99.3%	Gong and Duan (2010)
High Pressure Process Research Group, University of Valladolid (Spain)	Diameter = 74 mm Length = 1500 mm Material: porous sintered Alloy 600 Oxidant: air T. Flow: new water	t_R < 1 min Feed = 5–40 kg/h Air = 36 kg/h F_T = 10–72 kg/h T_R = 650 °C P = 23 MPa T_{FT} = 25–250 °C	Isopropyl alcohol, mixtures of isopropyl alcohol/acetic acid/crotonaldehyde, X_{TOC} > 99%	Bermejo (2005) and Bermejo and Cocero (2006a)
CEA Pierrelatte (France)	Diameter = 15 mm Length = 500 mm Material: porous α-alumina (0.8 μm) Oxidant: H_2O_2 T. Flow: water + H_2O_2	Feed = 3 kg/h F_T = 3 kg/h T_R = 450 °C P = 25 MPa T_{FT} = 380 °C	Mixtures dodecane/tributylphosphate, methanol removal rate > 99.5%	Fauvel et al. (2003a,b, 2004)
Pine Bluff Arsenal (USA)	Diameter = 121 mm Length = 3000 mm Material: Aerojet platelet AISI SS304 Oxidant: O_2 T. Flow: water	Feed = 150 kg/h T_R = 400–725 °C P = 24.8 MPa T_{FT} = 450 °C	Isopropyl alcohol, sugar and Na_2SO_4 solutions, military smokes and dye formulations, X_{TOC} > 99.9% (TOC < 5 ppm)	Rice et al. (2000)
Xi'an Jiaotong University (China)[a]	Diameter = 300 mm Length = 1600 mm Material: porous sintered AISI 316L Oxidant: O_2 T. Flow: water	Feed = 125 kg/h F_T = 40 kg/h T_R = 400–500 °C P = 25 MPa T_{FT} = 350–450 °C	Sewage sludge, X_{COD} = 99.6%, no obvious corrosion or salt deposition	Xu et al. (2010, 2012)
Sandia's EER (USA)	Diameter = 27.9 mm Length = 914 mm Material: Aerojet platelet AISI SS304 Oxidant: air T. Flow: water	Feed = 36 kg/h F_T = 37.8 kg/h T_{FT} = 450 °C T_R = 450–550 °C P = 25.5 MPa	Isopropyl alcohol, military smokes and dye formulations, no Na_2SO_4 deposition on the transpiring wall	Rice et al. (2000)

Notes: T. Flow = transpiring wall fluid, F_T = transpiration water flow rate (kg/h), T_{FT} = transpiration water temperature (°C), T_R = temperature in the reaction chamber (°C), t_R = residence time (s), Feed = organic wastewater entering the reactor (kg/h), and P = reaction pressure (MPa).

[a] Newly added information, and other information mainly refers to the literature (Bermejo et al., 2006a).

organic matter. Reactor corrosion and salt deposition properties under specific operation conditions for a certain feedstock also have drawn much attention. However, few reports explore the influential factors like the transpiration water distribution formation, the pressure difference between the two sides of the transpiring wall, the reactor construction, and the reaction fluid properties. Thus, it is necessary to systematically and thoroughly study the influence of these factors on TWR properties.

As mentioned before, the subcritical water film can re-dissolve precipitated salts and is more beneficial to protecting the transpiring wall. Hence, some studies set the transpiration water temperature at 40–250 °C (Wellig et al., 2005) or control it in the range of 125–200 °C (Príkopský et al., 2007). Nevertheless, subcritical water will remarkably reduce the reactor effluent temperature, making the heat recovery less efficient (Bermejo and Cocero, 2006b). The system energy efficiency is only about 31% when the feedstock temperature is in the range of 350–400 °C, the transpiration water temperature is in the range of 200–300 °C, and the transpiration water flow rate is half of the feedstock flow rate (Zhang et al., 2011a). Therefore, Abeln and Kluth (2002) suggest that transpiration water temperature shall be controlled at approximately 400 °C, while the researchers in ITC-CPV control the transpiration water temperature at 550 °C (Abeln et al., 2004). However, the supercritical water film cannot re-dissolve precipitated salts and meanwhile consumes much energy due to the higher preheating temperature. Thus, more research should be done to improve the heat recovery of TWR, and it is particularly essential to optimize the transpiration water temperature and flow rate.

Príkopský et al. (2007) use a TWR with a transpiring wall (3–5 μm pore size) to treat an artificial wastewater with up to 3 wt% Na_2SO_4, and no reactor plugging or a pressure drop increase across the transpiring wall is detected. Wellig (2003) employ a sintered metal transpiring wall with a pore size of 5 μm to avoid plugging, but Bermejo et al. (2006a) recommend that the pore size shall be bigger than 24 μm. According to the summarization regarding TWR construction sizes and operation parameters, the transpiration water temperature is in the range of 20–550 °C, and the transpiring wall pore size is controlled at 0.84–30 μm, and R is in 0.5–5. To date, the selection range of operation parameters is still too wide to theoretically instruct the TWR design and operation, so further research is required.

It is understandable that homogeneous and stable water film distribution can be obtained through the optimizations of TWR construction and operation parameters (Zhang et al., 2011b). However, according to the current study, detailed information about the formation and action process of transpiration water film is still scarce at present, resulting in the deficiency of regulation methods of effectively obtaining excellent water film properties. Without theoretical instructions on the TWR design and operation, it is difficult to generate a perfect transpiration water film. After being operated for some time, TWR will take place corrosion and plugging problems to some extent, which will remarkably effect its long-term safe running. Therefore, a more detailed study of the formation and action process of the transpiration water film is necessary to further optimize the operation parameters. Furthermore, it is also imperative that the long-term applicability of the SCWO-TWR plant in an industrial process by testing its safety, reliability, economic feasibility using the selected wastes.

2.4. Safety control

Continuous fluid flows through small pores to protect the transpiring wall by balancing the pressure difference between two sides of the transpiring wall. It meets the Darcy law when supercritical water flows through the porous wall (Fauvel et al., 2004). It has been mentioned that the sintered transpiring wall is fragile due to high temperatures even when it is constructed by metallic Ni-Alloy (Bermejo et al., 2011). Thus, the safety operation protection of the transpiring wall is very significant. It can judge whether the porous wall is plugged or destructed by the change of pressure difference between the two sides of the wall. Hence, Lee et al. (2005) install a pressure transducer and an additional pressure gauge at the reactor top to detect any possible damage of the transpiring wall or any liquid backflow phenomenon. Fauvel et al. (2004) online check whether the porous transpiring wall is good or not via measuring the pressure drop at the radial direction. Moreover, the pressure control valve must adopt an abrasion-resistant valve (Foster Wheeler, 2001), otherwise it will suffer from erodibility during solid-containing wastewater SCWO.

In the TWR (Xu et al., 2010), the transpiring wall with the filtering precision of about 30 μm and the surface density of 20% is made of sintered wire netting. 100 layers C276 metal nettings (44 μm pore size and 0.1 mm thickness) are bonded together and then sintered at a high temperature condition in a model to form the required transpiring wall. The expansion space of the transpiring wall is also provided for the heating operation process when it is installed in the reactor. A pressure balance plant with a taper sealing surface is equipped to eliminate the unsafely pressure difference of its two sides. As soon as the pressure difference is near the acceptable pressure limit value (0.5 MPa) probably due to pores plugging, the taper sealing surface will automatically open to protect the transpiring wall. In all of tests on the reactor, no any problem concerning the transpiring wall is found.

In the corresponding SCWO-TWR plant (Xu et al., 2012), both the preheating rate and the cooling rate of the reactor during the startup and shutdown period are controlled at below 60 °C/h in order to prevent the seal of the reactor flange from leaking in the next operation. The reactor pressure is adjusted by a back pressure valve and a safety valve is also set to protect the reactor. The temperature of the pressure-bearing wall can be controlled in a normal range by regulating the opening degrees of electric valves equipped on the reactor top and middle transpiration water pipelines, the heating power of the electric heater and the flow rate of the high pressure metering pump. The reactor top fluid temperature is determined and maintained by changing the heating power of the electric heater and the flow rate of cooling water entering the cooling coil in the reactor. Important parameters such as the reactor top fluid temperature, the reactor bottom fluid temperature, the reactor top cover temperature, the pressure-bearing wall temperature, the reactor pressure, the pressure difference of the transpiring wall, are displayed on the computer screen in the operation process. This helps to monitor and judge whether the TWR works under normal conditions. Major parameters like the flow rate of transpiration water and the reactor bottom fluid temperature can be adjusted through an automatic control interface. As soon as any value exceeds its originally set maximum value, the control interface will alarm with a sound and a red indication. If necessary, the corresponding fault shutdown procedure will be performed automatically. It has been proved that the TWR and the whole

plant are safe enough and no any danger appears in the operation processes.

It is better to operate and control a SCWO-TWR plant in a separate control room at a far distance for convenient operation and safe control under high temperature and high pressure conditions. However, this will undoubtedly increase the investment cost remarkably owing to the installations of electric valves and instruments with remote indication and/or control performances.

2.5. Economic analysis

It is agreed that TWR can effectively dispose high concentration, bio-refractory wastewaters with corrosive species and high salt contents. Using a SCWO-TWR system to treat halogenated organic compounds is competitive to other methods, and feedstock containing up to 5 wt% solid matters can be introduced into the reactor by a membrane pump (Abeln et al., 2001). However, except reactor corrosion and plugging problems, the industrial scale-up of a SCWO plant for real wastewater treatment has also been affected by the high operation cost (Vadillo et al., 2011). The operation cost is determined by adopted equipments, treatment capacity, concentrations and types of organic matters, operation conditions, staff costs and so on. Nowadays, all operation cost estimation data about SCWO show that 1 ton of wet organic waste with the organic matter content of 10 wt% costs no more than 300 dollars (Kritzer and Dinjus, 2001). Shen et al. (2010) have made an economic analysis for a SCWO-TWR system with the treatmemt capacity of 300 m^3/d, and state that the operation cost to deal with organic wastewater with the COD concentration of 40,000 mg/L is about 5.2 dollars/m^3, which is lower than those of conventional sanitary landfill and incineration means. Abeln et al. (2007) have reported that the operation cost of a 100 kg/h SCWO-TWR plant is about 659 euros/t which will be reduced to 380 euros/t if the treatment capacity is scaled up to 1000 kg/h. Of course, byproduct incomes such as surplus heat energy and CO$_2$ must be ensured in order to obtain a comparably low operation cost.

Oxygen is regarded as the most suitable oxidant in SCWO (Zhang et al., 2011b), and oxygen consumption cost is considered as the most important cost, particularly for some pilot-scale plants which run with OC = 2.0 (Kritzer and Dinjus, 2001). In fact, some research has proven that even excess oxygen of 5% may be sufficient for complete oxidation of organic matter (Alonso et al., 1999; Kritzer et al., 1999a,b). Thus a high OC is not necessary and is also not realistic for a prospective industrial application (Kritzer and Dinjus, 2001). The OCs used in the commercial SCWO plants developed by HydroProcessing (USA) and Chematur Engineering AB (Swede) for sewage sludge treatment are approximately 1.0 and 1.4, respectively (Gidner and Stenmark, 2001; Griffith and Raymond, 2002). Turbosystems Engineering (USA, 2008a) utilizes a OC of around 1.0–1.5 for their TWR. Thus, OC should be minimized as much as possible on the basis of the precondition that organic matters are destroyed thoroughly. It seems that OC should be controlled in the range of 1.0–1.5 if complicated facilities for excessive oxygen recovery are not installed in the SCWO-TWR plant. Otherwise excessive oxygen should be recovered to improve the SCWO's sustainable potentialities (Yang, 2003; Berm Svanström et al., 2004; An, 2010).

One of the main challenges of TWR is the energy recovery problem because reaction fluid is cooled and diluted by low temperature transpiration water. Especially, the reactor outlet temperature is remained at a subcritical temperature to maximize salts solubilities to avoid reactor plugging (Bermejo et al., 2006a). The mixed fluid temperature is about 450 °C if the transpiration water of 350 °C is mixed with the reaction fluid of 600 °C at the flow rate ratio of 0.4. Energy recovery in SCWO is commonly achieved by preheating feedstock through the high temperature reactor effluent via heat exchangers (Bermejo et al., 2009b; Lavric et al., 2005). In the SCWO-TWR system, heat can also be recovered enough by preheating feedstock and transpiration water. It has been reported that the energy efficiency of a SCWO-TWR system with the treatmemt capacity of 300 m^3/d can reach up to 56.4%. Whereas, Chen et al. (2010) confirm that the ratio of effective energy utilization is only close to 34.3% at certain conditions. It may augment with increasing organic matter concentration and/or decreasing OC, and both the reaction pressure and the disposal quantity also play crucial roles in the ratio. Increasing the transpiration water temperature and decrease its flow rate may also be helpful, but this is not good for the formation of an excellent transpiration water film. Probably surplus heat can be used to produce steam for electric generation or to form hot water for industrial application (Bermejo et al., 2009b; Bermejo and Cocero, 2006b; Cocero et al., 2002a,b). Obviously, the designs and combinations of heat exchangers require to be optimized to gain sufficient heat recovery for a low operation cost. Zhang et al. (2011b) conduct heat cascaded utilization via complicated heat exchanges combination. Therefore, it can be concluded that the methods of improving economy of the SCWO-TWR plant include increasing feedstock concentration, treatment capacity and byproduct income, and decreasing OC, reaction pressure and temperature.

3. Numerical simulations on TWR

Harsh reaction conditions such as high temperature, high pressure, and corrosive oxidation environment in a TWR make it hard to determine flow conditions and species concentrations. The flow patterns are quite too complicated to be described by ideal flow models from a physical standpoint (Plugatyr and Svishchev, 2008). Thus, quite few studies have been published on distribution properties of corrosive species, inorganic salts, or organic matter, etc. Numerical simulation is an important, low-cost research method in the new reactor development. Therefore, some researchers have adopted the computational fluid dynamics (CFD) technique to obtain more inside information related to the TWR. Oh et al. (1997) early report CFD simulations of a steady-state SCWO process. Narayanan et al. (2008) adopt Peng–Robinson equation to their CFD model to simulate a single phase combustion process for understanding the interdependent relations of various phenomena. Zhou et al. (2000) perform more detailed numerical simulations regarding SCWO using complete 2D (two dimensional) and 3D (three dimensional) models with all the important features. In the model of Bermejo et al. (2005), flow patterns are divided into mixer zone, upper zone and cooling zone. Moreover, the CFD simulation for methanol SCWO in a TWR with a hydrothermal flame shows that flow fields are greatly dependent on the reactor construction and its operation parameters (Lieball, 2003). According to model predictions, TWR can dispose a feed flow rate as high as 3000 kg/h and reagents can be injected at 25 °C (Bermejo et al., 2011).

Generally speaking, CFD simulation is an effective approach to investigate TWR, and most simulation results are in accord with experimental values. Sierra-Pallares et al. (2009)

report that the absolute average deviations of their CFD simulations on the temperature of the flame and its structure are below than 10% in most tested cases. The methodology combining a micromixing model along with the EDC (Eddy dissipation concept) model, predicts the flame structure with a temperature gradient similar to the experimental cases. Turbulent reactive CFD models have been validated by the comparison with measured data (Lieball et al., 2001, 2002; Lieball, 2003). Wellig (2003) confirms that his model can correctly predict the length of the supercritical region of his reactor. Anderko–Pitzer (AP) EoS, which has been described in the previous literature (Anderko and Pitzer, 1993), can accurately predict volumetric properties and phase equilibrium for aqueous systems at high temperature and high pressure conditions (Bermejo et al., 2007). On the basis of investigation results about reaction initiation of isopropanol SCWO (Bermejo et al., 2009a), Bermejo et al. (2011) also provide the methods and assumptions of the model construction as well as some specific calculation means. It is also believed that TWR scale-up can be successfully facilitated by creating numerical models, validating these models against the practically available experiment data, and then adopting the models to simulate the larger reactor performances (Bermejo et al., 2005). It may be attributed to that simulation results can show good agreement with limited experimental data (Oh et al., 1996).

It is clear that the computer simulation by CFD can complement SCWO experimental investigations. Narayanan et al. (2008) state a simple mathematical model can capture many features of a SCWO reactor, and simulation results are valuable not only for a clearer understanding of the phenomena but also for better experiment designs. The institute for reactor safety carries out 2D and 3D steady-state calculations to get an insight into local flow conditions and species concentrations inside the reactor and around the transpiring wall (Abeln et al., 2004). A simulation about the temperature profile and acetic acid compositions in a TWR indicates that the required time for completing reactions is very short and wastes concentration rapidly decreases, and products or intermediates quickly fill up the whole reactor (Bermejo et al., 2010). Li et al. (1991) point out that oxidation kinetics involves the formation and destruction of rate controlling intermediates, whereas some organic matters are directly converted into final oxidation products (Bermejo et al., 2011). Lieball (2003) performs a CFD simulation in order to obtain optimal flow conditions to avoid salt deposition, and wall protection is quantified by the thermodynamically allowable salt inlet mass fraction not leading to deposition, and the salt mass fraction can be calculated for any location in the reactor. His analysis displays that a high bulk flow temperature, a large bulk flow rate as well as a considerable R provide a more favorable flow field to maintain adequate kinetics for waste destruction.

However, complicated reactor configuration and operation conditions, as well as the difficulties to measure key factors characterizing the flow in the reactor, make corresponding CFD simulation very complex. An inappropriate model simplification may result in relatively big errors compared with experimental results. Lieball (2003) determines the optimum flow condition and suitable temperature distribution by a numerical simulation, whereas simulation results about the temperatures near the transpiring wall are not consistent with experimental data. Bermejo et al. (2007) detect notable discrepancies in the heat capacity calculation when conducting a comparison between the properties calculated by AP EoS

with those calculated via the Peng–Robinson EoS. Through a simulation, Narayanan et al. (2008) think that reactions can be controlled by changing the mixing ratio of fuel and oxygen, but the temperature at the reactor axial direction is about 15–18% higher than the really measured value. It is also noted that model simplification leads to a bigger inaccuracy for the simulation results on the maximum reaction temperature (Bermejo et al., 2010). Hence, there are still some comparatively big errors for some numerical simulation results about TWR, and it may be attributed to the unclear interaction processes such as flow, heat transfer and mass transfer in the TWR. For instance, for a TWR with a hydrothermal flame, there are several unknowns such as combustion modeling, material properties, and turbulence modeling (Narayanan et al., 2008). Accordingly, further improvement on the TWR mathematical models based on theoretical analysis and experiment investigations is needed.

For getting reliable simulation results, it is essential to further investigate mass and heat transfer, flow field, reaction kinetic, phase equilibrium and so on. Natural convection should not be neglected because it is affected by temperature and concentration gradients (Bermejo and Cocero, 2006b). It is also necessary to possess accurate thermodynamical properties data of water and aqueous mixtures under reaction conditions (Bermejo et al., 2007). Narayanan et al. (2008) point out that it needs further refinements to the model and more advanced simulation techniques like more detailed chemistry along with finite-rate kinetics. They also propose that the measurement of the turbulence intensity along the axis of the reactor is very useful for choosing the right turbulence model, or for simply recalibrating the standard k–ε model. Moreover, for a TWR with a hydrothermal flame, it significant to further study the ignition and extinction phenomena associated to hydrothermal flames and turbulence–chemistry interaction (Sierra-Pallares et al., 2009). These proposed investigations will help to improve the accuracy of CFD simulation results concerning TWR.

4.   Conclusions and outlook

This work objectively summarizes TWR characteristics, such as construction properties, combination with a hydrothermal flame, influences and utilizations of operation parameters, safety control, economic evaluation, and numerical simulations. Operation parameters optimizations, current problems and subsequent studies concerning TWR are also presented. Without the protection of an excellent water film, TWR will encounter corrosion and plugging problems to some extent after being operated for some time. It is still necessary to further optimize the operation parameters of TWR, and correspondingly to establish effective regulation and control methods to generate an excellent water film and meanwhile to ensure a proper energy efficieny. Moreover, it is necessary to test the long-term safety, reliability, and economic feasibility of the SCWO-TWR plant for the selected feedstock under the proposed full-scale operations. All this information is very valuable for guiding TWR design and operation and for promoting its extensive applications in SCWO systems.

Acknowledgments

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